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Non-monotonous temperature dependence of the spectral maximum of photoluminescence in CdS/ZnSe superlattices

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Abstract. Macro- and micro-photoluminescence (PL) spectroscopy is applied to investigate exciton localization in cubic CdS/ZnSe type-II superlattices (SL) in the temperature range between 5 K and 35 K. The non-monotonous shift of the macro-PL maximum with increasing temperature reveals the kinetic contribution of acoustic-phonon-assisted exciton hopping processes. The kinetic theory of localized excitons has been generalized from zero to finite temperatures allowing for exciton hopping from low-energy to high-energy localized sites as well as for the upwards-downwards correlation. The results of kinetic theory are compared with those of computer simulation and the experimental data.

In this work the properties of localized excitons of several cubic CdS/ZnSe superlattices have been investigated using spatially integrated (macro-PL) and spatially resolved (μ-PL) photoluminescence spectroscopy. The band alignment of this heterostructure is of type-II with the conduction and valence band off-sets of about 800 meV and 500 meV, respectively: the CdS (ZnSe) layers form the potential wells for the electrons (holes) [1]. We concentrate here on the macro- and μ-PL results of a 200 period (19 Å/19 Å) CdS/ZnSe superlattice grown by molecular-beam epitaxy on GaAs(001) [2]. The PL spectra discussed in the following were excited by the 351 nm line of an Ar^+-ion laser and measured with a spatial resolution of about 1 μm (μ-PL) or about 50 μm (macro-PL).

The macro-PL spectrum is displayed together with the PLE spectrum in the inset in Fig. 1. In Fig. 2(a) μ-PL spectra are shown, which have been recorded at two different temperatures. Besides a broad PL background, narrow line emission is observed which is typical for strongly localized excitons. Full circles in Fig. 1 show the measured temperature dependence of the relative shift for the macro-PL maximum

$$\Delta E_{\rm m} = \hbar\omega_{\rm m}(T) - \hbar\omega_{\rm m}(0) - \delta E_{\rm g}(T)\,, \qquad (1)$$

where $\omega_{\rm m}(T)$ is the spectral position of the PL maximum at the temperature T, $\delta E_{\rm g}(T)$ is the temperature shift of individual narrow lines in the μ-PL spectra which follows the temperature dependence of the SL band gap. The value of $\Delta E_{\rm m}$ obviously represents a purely kinetic contribution to the shift.

For numerical simulation we generated two-dimensional, random, uniform distributions of localization sites on a square cell of sufficiently large size with the chosen energy density of states, $g(\varepsilon)g_0 \exp(-\varepsilon/\varepsilon_0)$. The PL spectrum was calculated as a sum of contributions of individual localized sites, each one broadened by a Lorentzian. For the simulation of macro-PL spectra we generated ≥ 2000 configurations to obtain a sufficiently smooth spectrum. In order to take into account qualitatively the inhomogeneous broadening, the macro-PL

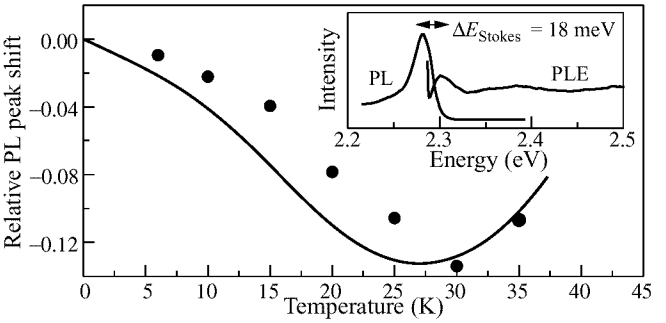

Fig. 1. Temperature dependence of the shift of macro-PL maximum defined by Eq. (1) and related to the low-temperature PL Stokes shift equal to 18 meV for a CdS/ZnSe (19 Å/19 Å) SL. Full circles, experiment; solid line, computer simulation. In inset: The PL and PLE spectra are compared revealing a Stokes shift of 18 meV.

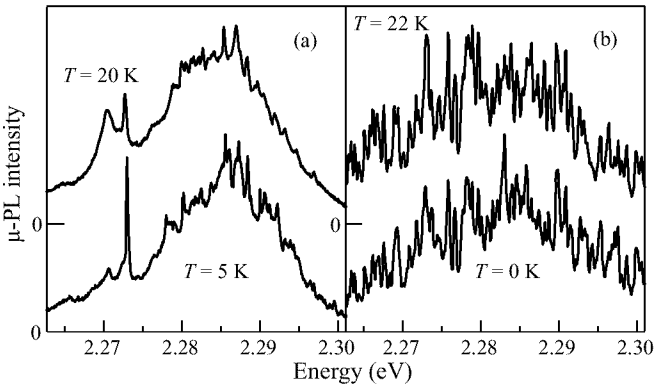

Fig. 2. (a) μ-PL spectra (spatial resolution $\approx$ 1 μm) measured from a CdS/ZnSe (19 Å/19 Å) SL at $T = 5$ K and 20 K. (b) Computer-simulated μ-PL spectra for $T = 0$ K and $T = 22$ K. The shift $\delta E_{\text{g}}(T)$ is ignored.

spectra, simulated for a fixed value of the exciton mobility edge E_0, were convoluted with a Gaussian describing the distribution of E_0. For the simulation of μ-PL spectra (see Fig. 2(b)) we took 200 subsystems each containing 100 localized-exciton sites randomly distributed with equal probability within a square area and with the weight $g(\varepsilon)$ in energy. The exciton mobility edge in each subsystem was chosen randomly in accordance with the Gaussian distribution.

The parameters chosen to calculate the PL spectra are as follows: $\omega_0\tau_0 = 3\times10^4$, $\pi(a/2)^2 g_0\varepsilon_0 = 0.2$ (the notations are the same as in [4]). The inhomogeneous broadening is described by the Gaussian with a width $3.6\varepsilon_0$. At zero temperature the PL maximum occurs at $E_0 - \hbar\omega_{\text{m}} = 3.76\varepsilon_0$. Since the PL Stokes shift equals 18 meV (see the inset in Fig. 1) we obtain for ε_0 the value $\approx$ 4.8 meV.

We have generalized the kinetic theory [3, 4] of localized excitons from zero to low but finite temperatures. At $T = 0$ each site is characterized by two parameters: the localization energy $\varepsilon = E_0 - E_{\text{L}}$ (E_{L} is the localized-exciton excitation energy E) and the distance r to the nearest lower-lying site. At finite temperature each site is characterized by three parameters, ε, ε' and r, where ε' is the localization energy of the optimum site for the local

hopping process. If the probability to occupy such a site is denoted by $f(\varepsilon, \varepsilon', r)$, then the energy distribution $N(\varepsilon)$ which determines the PL spectral intensity is given by

$$N(\varepsilon) = g(\varepsilon) \int_0^\infty d\varepsilon' \int_0^\infty dr P_\varepsilon(\varepsilon', r) f(\varepsilon, \varepsilon', r) . \tag{2}$$

Here $P_\varepsilon(\varepsilon', r)$ is the distribution of optimum neighbors in energy and space. We propose a rather simple and effective form of the approximate kinetic equation for $f(\varepsilon, \varepsilon', r)$ and write it as [3]

$$\left[\frac{1}{\tau_0} + \bar{w}(\varepsilon, \varepsilon', r)\right] f(\varepsilon, \varepsilon', r) - \tag{3}$$
$$- \int_0^\infty \int_0^\infty d\varepsilon_1 dr_1 \frac{g(\varepsilon_1)}{g(\varepsilon)} P_{\varepsilon_1}(\varepsilon, r_1) \bar{w}(\varepsilon_1, \varepsilon, r_1) f(\varepsilon_1, \varepsilon, r_1) = \Gamma_0 .$$

The notations used are as follows: τ_0 is the recombination time, Γ_0 is the generation rate from delocalized states, $\bar{w}(\varepsilon, \varepsilon', r) = w(\varepsilon, \varepsilon', r) p(\varepsilon, \varepsilon', r)$, $w(\varepsilon, \varepsilon', r)$ is the exciton transfer rate for the $\varepsilon \to \varepsilon'$ transition between the sites O and O' separated by a distance r; for $\varepsilon < \varepsilon'$, the factor $p(\varepsilon, \varepsilon', r)$ is set to 1 and, for $\varepsilon > \varepsilon'$ it is equal to the probability that near the sites O, O' there exists a localization site O'' satisfying the following two conditions: (i) the upward hopping process $O \to O'$ is more probable than the process $O \to O''$ and (ii) the hopping $O' \to O''$ is more probable than the downward process $O' \to O$. The factor p takes into account that, at nonzero but low temperatures, the major part of excitons which participate in the upwards transition $O \to O'$ return back from the site O' to the site O and either recombine on the site O or relax from O to other localization sites different from O'. Note that in [3] the difference of p from 1 is ignored.

In Fig. 3(a) we present the relative shifts of the PL maximum as a function of temperature calculated neglecting inhomogeneous broadening. The dashed curve is calculated by using numerical solution of Eq. (3) for $p \equiv 1$. One can observe a remarkable discrepancy of the dotted curve from the solid curve which is the exact result of computer simulation. The dotted curve in Fig. 3(a) is calculated by using the proposed approach to account for the upwards-downwards correlation. It shows a good agreement with the results of computer simulation. The calculated non-monotonous behaviour of the Stokes shift with temperature was reported by Zimmermann *et al.* [5] and Baranovskii *et al.* [6]. Physically, it can be explained taking into account that, at $T = 0$, the photoluminescence is dominated by

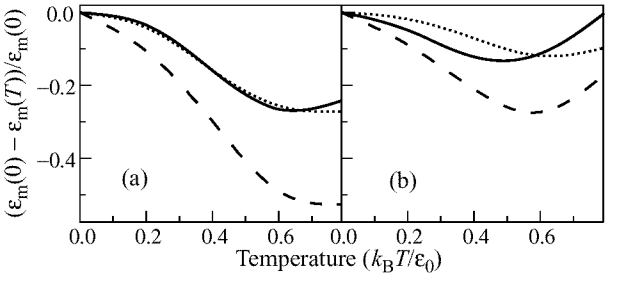

Fig. 3. Relative shift of the macro-PL maximum as a function of temperature calculated neglecting (a) and taking into account (b) inhomogeneous broadening. Solid lines, computer simulation; dotted lines, the proposed kinetic theory; dashed curve, the kinetic theory [3] which ignores upwards-downwards correlation.

excitons finding themselves on accidentally isolated localization sites acting as pores. For such sites the lifetime with respect to hopping to the nearest lower-energy neighbor exceeds the recombination time, τ_0. At finite temperatures, an exciton trapped by an effective pore has a possibility to be shaken down as it hops first to the nearest higher-energy neighbor and then to another lower-energy site. It is the factor $p(\varepsilon, \varepsilon', r)$ that estimates the probability for this possibility to be realized.

Figure 3(b) presents the temperature-induced shift of the PL maximum after the PL spectrum is convoluted with the Gaussian. The deviation between the solid and dashed curves can be interpreted in the following way. If the PL spectrum calculated for the homogeneous mobility edge is *symmetrical* with respect to the maximum then the inhomogeneous broadening makes no effect on the spectral maximum position. However, if the PL spectral maximum calculated for a fixed E_0 is *asymmetrical*, the inhomogeneous broadening results in a shift of the maximum position. At zero temperature the both calculated PL spectra almost coincide in shape. Hence the difference between the solid and dashed curves in Fig. 3(b) appears because the homogeneous macro-PL spectral shape is temperature dependent and, at final temperatures, asymmetries of the simulated PL spectrum and of that calculated by using the kinetic theory are different.

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